Dielectric Constant of Water Discovered to be Simple Function of Density over Extreme Ranges from – 35 to + 600°C and to 1200 MPa (12000 Atm.), Believed Universal

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ABSTRACT

The experimental static dielectric constants (ε) of water formulated by Fernández, et al., (1997-International Association for the Properties of Water and Steam, IAPWS), –35 to 600°C; 0.1 to 1200 MPa, are discovered to be closely described throughout by a simple equation of density (ρ), presented here, and agreeing with their reported calculated (extrapolated) values to 923°C. *Eight* limiting boundary conditions are observed. Values of ε follow isothermal straight-line slopes of log (ε – 1) vs log ρ down to densities of 0.25 g cm^{-3} water, even in dioxane-water solutions. At lower densities, all slopes curve asymptotically in approaching unity, while becoming unity throughout at –35°C (near metastable freezing point). Slopes above 0.25 g cm^{-3} asymptotically approach 1 2/3 at high temperatures that numerically proportionates (ε – 1) to volume times surface densities, with a proposed explanation given. Values for ε of water dissolved in dioxane down to 0.006 g cm^{-3} water (25-300°C) and in benzene to 0.014 g cm^{-3} water (300-400°C) extend uninterrupted from those for pure water. The Deul-Franck (1984, 1991) values of ε for benzene (25-400°C; to 400 MPa) by the relationship fall on a single straight-line *independent* of temperature. Theorists should evaluate this simple relationship of water and other liquids to density that appears to be universal.

I. INTRODUCTION

The static dielectric constant (ε), or static relative permittivity, of liquids is a property applied since the early 1900's to theoretical evaluations of electrolyte solutions. Before 1950, there were numerous published values of ε below 100°C. With values for water needed at higher temperatures, Franck in his pioneering studies on ionization of aqueous 1-1 electrolytes to very high temperatures and pressures [1-3] developed an equation for estimating ε, with Quist and Marshall[4] later presenting an equation extending its range. [These first equations of Franck[2] and Quist and Marshall[4] still provide reasonable values of ε at extreme conditions.] After 1965, numerous experimental and calculative studies on ε for water at high temperatures and pressures were made, as evaluated in the 1997 comprehensive formulation of Fernández, Goodwin, Lemmon, Levelt Sengers, and Williams[5], relying on the extensive database from Fernández, Mulev, Goodwin, and Levelt Sengers[6].

In determining ionization of NaCl in dioxane-water solutions at 100°C and pressures to 400 MPa, Yeatts, Dunn, and Marshall[7] plotted log (ε – 1) vs. log ρ_w to give isothermal straight lines to low water concentrations. They used this relationship in extrapolating to high temperatures. By applying here the Fernández, et al.[5], results, presented as a Release (standard) by the International Association for the Properties of Steam IAPWS)[8], a search for physical simplicity in dielectric-constant behavior was made over the wide ranges of temperature and density. Many theoretical equations describe the dielectric constant for water with limited success over short ranges of density and temperature.[5] The simple relationship presented here, however, universally describes its behavior over *all* experimental ranges of temperature and density with a minimum of required constants. With this success, it would seem that any theory must be based on its framework in applying Occam's razor.

II. UNIVERSAL DESCRIPTION OF DIELECTRIC CONSTANT FOR WATER AS SIMPLE FUNCTION OF DENSITY

A. General observations

Earlier, in searching for a rational description of dielectric constant (ε) as a function of water density (ρ_w) in dioxane-water solutions Yeatts, Dunn, and Marshall[7] applied ($\varepsilon - 1$) rather than ε, where here ε is the observed dielectric constant for either a solution or pure liquid and ε_w specifically is for pure water or its presence in a solution. As ρ of a substance approaches zero, by dilution or decreasing pressure for a gas, ($\varepsilon - 1$) must also approach zero whereas ε (a ratio of substance capacitance to that of a vacuum under the same condition) approaches unity. Straight lines were obtained by plotting isothermally $\log(\varepsilon - 1)$ versus $\log \rho$ (H_2O) in dioxane-water solutions[7] down to 0.10 weight fraction water where the low contribution to ε from dioxane in solution was neglected compared to that for water. The observed straight-line behaviors allowed extrapolations to obtain ε for theoretical application in calculating ionization constants of electrolyte solutions[7] over the ranges of experiment.

The recent comprehensive evaluation by Fernández, et al,[5] of all published values of dielectric constants for water from -35°C (near metastable freezing) to 600°C and at pressures to 1200 MPa has provided the best available values of the dielectric constant of water. Based on extensive theoretical considerations, Fernández, et al., also presented a fitting equation for this evaluation and gave table values of ε from -35^o to 927°C and from 1 to 1200 MPa. Representative values from the Fernández, et al., equation are described here isothermally in Fig. 1 as $\log(\varepsilon - 1)$ versus $\log \rho$, where for their listed values as a function of pressure the IAPWS Formulation 1995 of steam tables[9] was applied for conversion to density. The curves shown are actually calculated by Eq. (2) below that closely reproduces the Fernández, et al., equation values [Table I, Fig. 3, discussed later]. Included also in Fig. 1 are representations at temperatures from -35^o to 300°C far below the

possible densities for pure liquid-water, and that closely follow ε (water) in dioxane-water (25-300°C) and benzene-water (300-400°C) solutions (Section IV). Fig. 1 indicates at -35 to 927°C that isothermal curves at densities decreasing below 0.25 g cm^{-3} approach limiting slopes of unity. At densities from 0.25 to above 1.10 g cm^{-3} the slopes, $[\partial \log (\varepsilon - 1)/\partial \log \rho]_T$, are isothermally constant (Fig. 1). They increase sharply from 1.0 at all densities near -35°C (metastable liquid) to approach a limiting value of 1 2/3 above the liquid-vapor critical temperature of 374°C (Fig. 2).

B. The equation

For application and extrapolation based on the observed relations in Figs. 1 and 2 an equation was developed, by applying non-linear least squares (NLLS)[10], to describe the extensive compiled values of ε of Fernández, et al.[5], with added extrapolations, from -35° to 1000°C (238 to 1273 K) and at densities from approaching 0 to above 1.1 g cm^{-3}. The four-constant equation is given,

$$\log (\varepsilon - 1) = A\ Y + B\ (1 - Y) + [\ 1 + Y\ (S - 1)\ ] \log \rho + 3\ (1 - Y) \qquad (1)$$

where ε = dielectric constant, ρ = density / (g cm^{-3}), and (below) T = temperature/kelvins,

$$Y = 1 / (1 + 0.0012 / \rho^2)$$

$$A = \log (\varepsilon - 1) \text{ at } \rho = 1.0 \text{ g cm}^{-3}$$
$$= 0.7017 + 642.0 / T - 1.167 \text{ x } 10^5 / T^2 + 9.190 \text{ x } 10^6 / T^3$$

$$B = \log (\varepsilon - 1) \text{ at } \rho = 0.001 \text{ g cm}^{-3}$$
$$= - 2.710 + 275.4 / T + 0.3245 \text{ x } 10^5 / T^2$$

and

$$S = [\partial \log (\varepsilon - 1)/\partial \log \rho]_T \text{ at densities from 0.25 to above 1.1 g cm}^{-3}$$
$$= 1.667 - 11.41 / T - 3.526 \times 10^4 / T^2$$

Eq. (1) reduces to the form,

$$\log (\varepsilon - 1) = Y [\, C + (S - 1) \log \rho \,] + D + \log \rho \qquad (2)$$

where

$$C = A - B - 3$$
$$= 0.4117 + 366.6 / T - 1.491 \times 10^5 / T^2 + 9.190 \times 10^6 / T^3$$

and

$$D = B + 3$$
$$= 0.290 + 275.4 / T + 0.3245 \times 10^5 / T^2$$

Eq. (2) reproduces the values of ε in Tables 9, 12, 19, and 20 of Fernández, et al.[5], over their full range of temperature, density, and pressure predominantly to within the estimated absolute uncertainties stated in their Table 9 and text [$\Delta\varepsilon$'s of 0.05-0.3, but with some exceptions at –35°C and at densities above 1.1 g cm^{-3} at 0° and 50°C - discussed later]. IAPWS accepts their results as an official Release (1997)[8] in giving its credibility to the evaluations. Table I compares values of ε calculated by Eq. (2) with those at various state points included in both the IAPWS Release[8] and Fernandez, et al.,[5] paper showing the close agreements. The simple four-constant Eq. (2) was developed to reproduce the Fernández, et al., formulation in obtaining physical correlations for further evaluation as discussed in Sections IV-VI.

By applying Eq. (2) at densities from 0.25 g/cm^3 to above 1.1 g cm^{-3} , *Y* within uncertainty becomes unity and Eq. (2) reduces to the following two-constant Eq. (3), again providing values predominantly within the uncertainties estimated by Fernández, et al., and in the IAPWS Release:

$$\log (\varepsilon - 1) = A + S \log \rho \qquad (3)$$

Limited to 0.25 to 1.1 g/cm^3 and – 35^o to 923^{o}C

At water densities below approximately 0.003 g cm^{-3}, with *Y* now closely zero, Eq. (2) reduces to one-constant Eq. (4), again providing the same agreement with the Fernández, et al., equation and IAPWS Release:

$$\log (\varepsilon - 1) = D + \log \rho \qquad (4)$$

Limited to densities below 0.003 g cm^{-3} and from – 35^o to 923^{o}C

C. Consideration of required constants

At constant temperature four constants are needed for describing (ε – 1) as a function of density, with *Y* independent of temperature and significantly needed only at densities between 0.003 and 0.25 g cm^{-3}. The three constants (*A, B, S)* are quantitatively calculated as simple functions of temperature that, including *Y*, make a total of eleven needed constants for description over the entire range of density and temperature. These eleven constants reduce to seven at water densities above 0.25 g cm^{-3} and three when below 0.003 g cm^{-3} in applying Eq. (3) or (4). The eleven constants needed for universally describing (ε – 1) with both density and temperature can be compared to the twelve coefficients and twenty-two exponents applied in the IAPWS formulation[5, 8].

D. Deviation comparisons; questioning the IAPWS formulation at – 35°C and at densities above 1.10 g cm^{-3} at 0 and 50°C

Fig. 3 gives a deviation plot, $\Delta\varepsilon$ [IAPWS Eq. – Eq. (2)] vs (ε – 1) over ranges from – 35° to 927°C and 0.1 to 500 MPa (up to 1.1 g cm^{-3}) showing deviations predominantly less than 0.25 units. There is no observed trend away from the relation of Eq. (2), lending credibility to this equation. Table 1 presents comparative values for the several state points presented by Fernandez, et al., in their Table 9,[5] in essentially full agreement, but with three exceptions as follows.

At densities rising from 1.1 to 1.2 g cm^{-3} (– 35° to 300°C, 500 to 1000 MPa), the Fernández, et al., formulation values for ε suddenly increase by +1 to +3.5 units (+1 to +3.5%) from following the straight-line of log (ε – 1) versus log ρ. The good fit by the IAPWS formulation to Eq. (3) over a 340% increase in density (0.25 to 1.1 g cm^{-3}) followed by this sudden divergence in the next 9% increase in density (1.1 to 1.2 g cm^{-3}) is puzzling. The only data at these high densities and extreme pressures were those of Lees,[11] where difficulties in trying to reach these extreme conditions could have arisen. This anomalous, sharp divergence suggests possible small uncertainties in accuracy in the Lees data at his highest pressures of measurements. One might compare the straight-line behavior of benzene and other organics extending to high pressures without divergence, discussed in Section V.

Increasing the pressure on a fluid normally will increase its viscosity, which at high densities should increase rigidity of molecular movement. An increasing rigidity if significant would seem to *decrease* values of (ε – 1) from a possibly expected behavior [Eq. (3)] rather than increase them, as observed by the Lees values. Although for a different property, log K_w(ionization product, water) follows the straight-line form of Eq. (3) even to 13300 MPa[12]! Also, at the lowest temperature (–35°C) an increase by the Fernandez, et al., value from Eq. (3) was +3.1 units (+3.1%), not shown on Fig. 3. Comparative

calculated values of ε from the Bradley-Pitzer[13] formulation listed by Fernández, et al.[5], differ by only – 0.57 at – 35°C (0.1 MPa) and – 0.91 and – 0.72 at 0° and 25°C, respectively (both near 1.25 g cm^{-3} and 1000 MPa), agreeing well with Eq. (3). Thus calculated values of ε by Eq. (3) compared to representative state values from the Fernández, et al.,[5] - IAPWS[8] formulation (Table I) agree closely with estimated uncertainties except at – 35°C and at 0° and 50°C at densities near 1.25 g cm^{-3}, where instead agreement is good with the Bradley-Pitzer[13] formulation as shown in Table I. The above observations and rationalization suggest possible inaccuracy in the IAPWS formulation at these particular extremes.

E. Behavior of a defined polarization affinity with temperature and density

A polarization affinity (*PA*) is introduced here as a new property and defined as the quantitative increase in (ε – 1) with unit increase in density/(g cm^{-3}) at constant temperature. *PA* is expressed as $[\ \partial(\varepsilon - 1) / \partial\rho\ ]_T$ and derived from Eq. (2) or the even simpler Eqs. (3) or (4) for their respective ranges of applicability. The calculated values of *PA* at several constant densities are plotted in Fig. 4 as log *PA* against 1/(*T*/K) to show the quantitative relations and symmetrical curves obtained, with slopes at a given temperature suggesting application of the van't Hoff equation,

$$[\ \partial \log PA / \partial\ (1/(T/\mathrm{K})\ ]_\rho\ =\ -\ \Delta H / (2.303\ R) \qquad (5)$$

where R = gas constant

in obtaining a ΔH of increased polarization by increased density. The example for ΔH given in Fig. 4 shows a roughly – 2.1 kcal/(g cm^{-3}) for ΔH at the lowest temperatures and up to moderate densities with an absolute decrease to an apparent limit of zero near -35°C and unit density.

PA relates to the ease of inducing liquid-polarization by increasing density as reflected in the relative increase in dielectric susceptibility at a given temperature and

density. Fig. 4 shows a high *PA* at high densities and low temperatures that progressively decreases as temperature rises and density decreases. Thus, induced polarization becomes increasingly difficult to achieve as the kinetic energy rises and water density decreases. One also observes in the plots the asymptotical approaches to limiting straight-line slopes at the approach to infinite temperature, with approaches to a single common value at all densities at or near the metastable freezing point.

F. Eight observed limiting conditions supporting validity of Eq. (2)

Inspecting Figs. 1, 2, and 4 show eight limiting conditions when the Fernandez, et al.,-IAPWS values[5, 8] are described by the form of Eq. (2). These figures represent the dielectric constant in two dimensions as functions of temperature and density. Fig. 1 shows the two isothermal boundary limits with density at the approach to both zero and the highest density (limits 1, 2).

Fig. 2 shows the two limits of the isothermal slopes at high densities in approaching asymptotically a limiting value of 1 2/3 as temperature approaches infinity (limit 3) and a value of unity near the lowest possible temperature of liquidity (limit 4).

Fig. 4 shows $PA = [\, \partial(\varepsilon - 1) / \partial(\rho) \,]_T$ (as log *PA*) merging to a common value for all densities near the lowest temperature of (metastable) liquidity (where $S = 1$ throughout) (limit 5). The differing slopes of log *PA* vs. 1/(*T*/K) at constant densities asymptotically approach limiting slopes as temperature approaches infinity (limit 6). Moreover, ΔH of change for *PA* approaches a limit of zero at or near 1 g cm^{-3} near the lowest temperature of liquidity (limit 7).

The observed behavior at densities up to 0.003 g cm^{-3} further idealizes in that a single common curve (Fig. 4) describes log *PA* vs. 1/(*T*/K) (limit 8). This results from *S* being near unity simplified by Eq. (4) in describing this limiting low density range. At densities higher than 0.003 g cm^{-3} the quantitative form of a curve at constant density depends on the density applied as described by Eq. (2). These eight observed limiting conditions in the description of dielectric constant and their application in obtaining the

constants of Eq. (2) provide strong support for both the descriptive and potentially applicable theoretical validity of Eq. (2) and its additionally simplified Eqs. (3) and (4).

III. APPARENT NORMAL BEHAVIOR NEAR AND AT CRITICAL POINT OF WATER

Calculation of the dielectric constant at the liquid-vapor critical point (374^{o}C, 0.322 g/cm^3, 22.2 MPa) of water with Eq. (2) or (3) gives ε = 5.73, which compares with 5.36, or $\Delta\varepsilon$ = 0.37, from the Fernández, et al.,[5] (IAPWS[8]) formulation or by interpolation and extrapolation from their Table 20. Experimental determination of ε at the critical point would be extremely difficult because of infinite fluid compressibility. Nevertheless, values of ε from the Fernández, et al., and IAPWS Release established over regions near the critical point indicate consistent (no anomaly) normal behavior, as Fernández, et al., have emphasized, even though there are strong anomalies in pressure-volume-temperature (*PVT*) behavior.[9] Also, establishment of the ionization constant of NaCl [*K*(NaCl)] at the critical point from interpolation from near regions of *PVT* indicates dependence only on density and temperature.[14] Obtaining essentially the same value for *K*(NaCl) at the critical point from evaluation of ionization behavior along the liquid-vapor critical curve for NaCl-H_2O provides additional evidence for this dependence only on density and temperature.[15] Thus, both dielectric constant and electrolyte ionization behavior seem to be simple functions of density and temperature and not affected by strongly anomalous behavior of *PVT* near the critical point, discussed elsewhere.[14]

IV. DIELECTRIC CONSTANT OF WATER TO EXTREME DILUTIONS IN DIOXANE-WATER AND BENZENE-WATER SOLUTIONS; COMMON CURVE WITH PURE WATER

A. General observations

Several early studies in the 1930's-1960's presented very accurate measurements of dielectric constants in dioxane-water solutions at 25-50°C. Notable studies are those of Akerlöf[16], Fuoss and Krauss[17], Kunze and Fuoss[18], and Büttner and Heydtmann.[19] Generally, these measurements were made to apply the theories of Debye-Hückel and Born in evaluating ionization constants of electrolytes in dioxane-water solutions. In later evaluations of these behaviors, Marshall and Quist[20,21] discovered that upon considering dioxane as an "inert" diluent of water, an isothermal plot of log K (an ionization constant) against log ρ_w (density of water in solution) in dioxane-water solutions gave a straight line of slope value (n) proposed to represent the net increase in average effective solvation number upon ionization, as earlier interpreted and observed by Franck for ionization in supercritical water.[1-3] This observation and interpretation contradicted application of the Born theory widely applied at the time but which did not show its expected straight-line correlation of log K versus $1/\varepsilon$ over wide ranges of ε. Shortly after, Yeatts, Dunn, and Marshall[7], and Yeatts and Marshall[22] required values of ε for their theoretical evaluations in studies of ionization in dioxane-water solutions to 300°C. Extending from the above reasoning for the behavior of ionization constants in dioxane-water, they discovered that isothermal plots of log $(\varepsilon - 1)$ versus log ρ_w produced essentially straight lines to low concentrations of water in dioxane-water and they applied this correlation for direct application and extrapolation for use to 300°C.

B. Correction factors for ε of organic component in dioxane-water and benzene-water solutions; general application to non-polar organic liquids in highly polar solutions

In this study, as in the Fernández[5], et al., evaluation, we consider only the macroscopic ε as opposed to a microscopic ε related to close molecular interactions. This macroscopic ε represents a ratio of the electrical capacitance of a contained substance to that of a vacuum under the same conditions. Thus, in a liquid or gas, as the density decreases to zero the value of ε reaches unity. For studies of fluids at very low densities or for very low values of ε, the rational function for a polar liquid such as water (w) in solution with an essentially non-polar liquid such as dioxane would be ($\varepsilon - 1$), which would approach zero as ρ_w approaches zero where $\rho_w = \rho$(solution) times weight fraction water (X_w) and where the contribution of non-polar component to ε is neglected. This function was proposed and applied earlier for the needed behavior of ε_w in our studies of the ionization constant [K(NaCl)] of NaCl in dioxane-water[7]. It produced isothermal straight lines for log (ε - 1) vs. log ρ_w to moderately low water concentrations in contrast to a curve when plotting log ε against log ρ_w. These earlier studies were not needed at extreme dilutions of water, and the subtraction of an ε(dioxane) contribution from ε(observed) was insignificant and not done.

However, pure dioxane [a symmetrical diethylene dioxyheterocyclic ether, $O(CH_2CH_2)_2O$] at 25°C and 0.1 MPa gives $\varepsilon = 2.10$[16], and pure benzene gives a value near 2, with the exact value for benzene depending upon temperature and density.[23,24] Thus a correction for ε (dioxane) or ε (benzene) must be made for extrapolating to very low water concentrations in dioxane-water or benzene-water solutions for providing a rational descriptive behavior where the limiting condition is ε for non-polar solvent at the given T and P. Without experimental values of ε for pure dioxane as a function of T and P, the value of 2.10 was applied as an approximation at higher temperatures at dioxane liquid-densities close to 1 g cm^{-3}, seemingly a reasonable assumption for this symmetrical

molecule. Values of ε for pure benzene at high T and P were available from the extensive study of Deul and Franck[23,24] to 400°C and 300 MPa.

C. Correction for dioxane or benzene solvent required for ρ_w below 0.20 g cm^{-3}

A correction term, $(\varepsilon_{po} - 1)X_o$, for dioxane or benzene solvent was necessary at water densities below 0.20 g cm^{-3}, where $\varepsilon_{po} = \varepsilon$ for pure organic (dioxane or benzene) and X_o = weight fraction of dioxane or benzene. This term was subtracted from $(\varepsilon_{obs} - 1)$ where ε_{obs} is that observed for the solution. At the limit of pure dioxane or benzene, the total function, $[(\varepsilon_{obs} - 1) - (\varepsilon_{po} - 1)X_o]$, equals zero, while the function reaches $(\varepsilon_{obs} - 1)$ at the other limit of pure water where X_o equals zero. The full Eq. (6) is given,

$$\log (\varepsilon_w - 1) = \log [(\varepsilon_{obs} - 1) - (\varepsilon_{po} - 1) X_o] \qquad (6)$$

but with another term (G) required at water densities below 0.014 g cm^{-3}discussed next.

Applying Eq. (6) (with G discussed below) in subtracting the contribution by inert solvent (dioxane or benzene) from the measured $(\varepsilon_{obs} - 1)$ produces a constant slope to very low water concentrations at 25-400°C (Figs. 5 and 6), with the curvature at the lowest water concentrations following that from Eq. (2) for pure water. The uncorrected function $(\varepsilon_{obs} - 1)$ shows curvature at somewhat higher water concentrations than observed in Figs. 5 and 6. However, another correction term (G) is needed at extremely low water concentrations, discussed next.

C. Additional term for ε_w at extreme dilutions below 0.014 g cm^{-3} water

An additional term was needed for accurately describing ε_w for benzene-water at extremely low water densities below 0.014 g cm^{-3} although applied without effect (not needed) for the dioxane-water solutions to 0.006 g cm^{-3} water. After many calculative tests,

the following correction multiplier to the organic-component subtraction term provided the best fit with the adjustable parameter *F*, as discussed below,

$$G = (1 + F\rho_w) \qquad (7)$$

and included in the full Eq. (8) for log (ε_w - 1) that now describes log (ε_w – 1) over the entire range of water-organic compositions and superimposes values for pure water at water densities varying with pressure,

$$\log (\varepsilon_w - 1) = \log [(\varepsilon_{obs} - 1) - G (\varepsilon_{po} - 1) X_o] \qquad (8)$$

Substituting mole fraction for weight fraction in Eqs. (6) or (8) did not provide an acceptable fit for either the dioxane-water or benzene-water data. Since introducing an "inert" organic liquid *masks* the contribution of ε_w when compared to that for pure water, the relative *mass* of "inert" liquid (X_o) rather than relative number of molecular weights (mole fraction) would seem to be the rational choice. This choice of weight fraction seems to be confirmed by applying Eqs. (6) or (8). Considerations here can be applied to any non-polar organic component dissolved in water or any other highly polar liquid.

The term *G* may be considered an enhancement multiplication-factor to ($\varepsilon_{po} - 1)X_o$ without which ε_w is calculated increasingly too high when X_o closely approaches unity. The full term, $G(\varepsilon_{po} - 1)X_o$, reaches ($\varepsilon_{po} - 1$) for pure organic and zero for pure water [Eqs. (6) and (8)]. Values of *F* determined for dioxane-water did not correlate well with temperature (25°-300°C) probably because at 50°-300°C the range of data with consequent uncertainties did not extend to a sufficiently low concentration of water. With little effect on description, *F* was set equal to zero for the dioxane-water solutions (*G* = 1 throughout) and from NLLS[10] estimates smoothed to equal 5.0, independent of temperature, for benzene-water as plotted in Figs. 5 and 6 and discussed below.

D. Dielectric constant for water in dioxane and benzene solutions extending and superimposing behavior for pure water

Figs. 5 shows plots of log $[(\varepsilon_{obs} - 1) - G(\varepsilon_{po} - 1)X_o]$ vs log ρ_w derived from many published values for dielectric constants of dioxane-water and benzene-water solutions[7,16-26] and of pure water[5,6], with F [Eq. (7)] equal 0 for dioxane-water and 5 for benzene-water. Included are full lines calculated by Eq. (2) that significantly extend from and accurately reproduce the Fernández, et al., range of values for pure water. Fig. 6 shows an analogous plot to those in Fig. 5 of log $(\varepsilon_w - 1)$ applying Eq. (8) vs log ρ_w for benzene-water at 400°C, treating the excellent data of Deul and Franck[23,24] at extremes of pressure and over a range of water concentration. Also shown are the overlapping values for pure water from both Deul and Franck[23,24] and the Fernández, et al.,[5] Release by IAPWS.[8]

Calculated values of log $(\varepsilon_w - 1)$ in either dioxane or benzene solutions produce a common curve with log $(\varepsilon - 1)$ for pure water calculated by Eq. (2). Not only are the straight-line portions for pure water followed but also the curvature at very low water concentrations (Figs. 5 and 6). These agreements lend further support to the considerations and applications of Eqs. (1)-(4), (6), and (8).

By applying Eqs. (6) or (8) to these observed values, with $F = 5$ for benzene (zero for dioxane), the values of log $(\varepsilon_w - 1)$ obtained from the several groups of log $(\varepsilon_{obs} - 1)$ are shown to merge closely on the curve for pure water [Eq. (2)] with little distinction as separate groups. Each group is of the same weight-composition with changes in a group caused by pressure increases to 300 or 400 MPa. Fig. 7 includes plots applying actual tabulated values of ε for water of Fernández[5], et al., at 50, 387 and 927°C to show their agreement with the continuous line of Eq. (2), and compares these plots with values of Leong and Dunn[24] for dioxane-water at 50°C. There is perfect agreement at 50°C between the water and dioxane-water solution values. These plots show on an expanded scale the

relative displacements with respect to temperature and density, and emphasize the parallel behavior with the dielectric-constant behavior of pure water at the high temperatures.

At 25-400°C in Figs. 5 and 6, there is indeed curvature at water densities below 0.25 g cm^{-3} in agreement with Eq. (2) for describing pure water at extremely low densities that shows the expected approach to unity of $[\partial \log (\varepsilon - 1)/\partial \log \rho]_T$ as ρ_w approaches zero (Fig. 1). Without correcting for dioxane or benzene in solution, however, a deviation from the straight line at low water concentrations would be sharply greater, and there would be no correlation with Eq. (2) developed only from the behavior of pure water from Fernandez, et al.[5] This same change in slope approaching unity is thus seen in Fig. 1, with an expanded range from high to moderate densities in Fig. 7 for pure water at 387-927°C.

Fig. 8 provides greater detail at densities above 0.4 g/cm^3. The values of dielectric constants for dioxane-water solutions at 100° and 300°C applied in Figs. 5 and 8 actually were extrapolated from those at 80°C and below as detailed in the earlier studies[7,22,26] because high temperature experimental values were not available then or now. The slope at 25°C in the high range of log ρ_w [ρ_w above 0.1/(g cm^{-3})] from the early experimental data for dioxane-water solutions agrees and overlaps perfectly with the later evaluated experimental studies in pure water.[5] The earlier tabulated estimates of ε for dioxane-water applied at both 100° and 300°C were for pressures from vapor saturation to 400 MPa, while the experimental values for benzene-water at 300°C were at pressures from saturation to 170 MPa. These values give within uncertainty the same slopes from the pure water straight-lines at 100° and 300°C evaluated from the Fernández, et al., results estimated to 1200 MPa! The overall agreement from 25° to 400°C (Figs. 5-8) seems excellent, remembering that all dielectric constants for dioxane-water were obtained 25 to 75 years before and those for benzene-water 13 years before the 1997 Fernández, et al., compilations for pure water and subsequent IAPWS Release!

Fig. 9 shows a deviation plot for $\Delta\varepsilon_w$ [Eq. (6) minus Eq. (2)] with $F = 0$ for dioxane-water solutions [Eq. (8) reduces to Eq. (6)] and $\Delta\varepsilon_w$ [IAPWS Eq. – Eq. (2)] for pure water versus ($\varepsilon_w - 1$) at 25°C at densities of water from 0.006 g cm^{-3} to 1.2, showing a remarkable average agreement of about ± 1 unit in $\Delta\varepsilon$! While there is greater scatter in the dioxane-water data than for pure water there is no trend away from adherence to Eq. (2). When one considers that the measurements applied at the extremely low concentrations were published more than 70 years ago, and the other studies many years before the Fernández, et al., evaluations, there can be no prejudice involved in the agreements.

The experimentally observed dielectric constants for the organic-water solutions (ε_{obs}) can be described by substituting Eq. (6) or (8) for log ($\varepsilon_w - 1$) into Eq. (2) for log ($\varepsilon - 1$) and solving for ε_{obs}. Thus ε_{obs} can be calculated throughout the range of water-organic compositions, thereby enhancing the simplicity of description and again emphasizing the fundamental significance in applying density.

E. The Deul-Franck values of ε for benzene-water at 300-400°C

Figs. 5, 6, and 8 showing the agreement in following Eq. (2) for pure water of the excellent data of Deul and Franck[23,24] for benzene-water solutions at 300° to 400°C and to 280 MPa versus log ρ_w to solution water densities lower than 0.01 g cm^{-3} is remarkable. Values of (ε_w - 1) at this lowest water density approach zero, or for ($\varepsilon_{obs} - 1$) approach that of pure benzene. At the lowest experimental water density (0.015 g cm^{-3}) shown in Fig. 6, ε_w from Eq. (8) differs by only 0.03 units from that calculated by Eq. (2) for pure water.

V. ORGANIC LIQUIDS FOLLOWING STRAIGHT-LINE FORM OF EQ. (3)

A. General behavior at low temperatures to high pressures

Several investigators[27-30] in earlier years made many measurements of the dielectric constant of pure organic liquids at low temperatures as a function of pressure (density). I have plotted the measured dielectric constants of organic liquids obtained by Danforth,[27] Chang,[28] Mopsik,[29] and Schornack and Eckert[30] as log ($\varepsilon - 1$) vs. log ρ at constant temperatures ranging from -50° to +75°C for these separate liquids according to Eq. (9) [form of Eq. (3)], and obtained the constants $A^{\ddagger}$ and $S^{\ddagger}$ by NLLS[10]

$$\log (\varepsilon - 1) = A^{\ddagger} + S^{\ddagger} \log \rho \qquad (9)$$

These plots give fully constant slopes (straight lines) as observed in the high-density water range for water (Fig. 1) and for dioxane-water and benzene-water solutions (Figs. 5-8) discussed in Section V. The straight-line isothermal slopes ($S^{\ddagger}$) obtained vary from 1.0 to 2.0 for the many liquids studied [carbon disulfide, diethyl ether, pentane, chlorobenzene, bromobenzene, hexanol, ethanol, t-butanol, glycerin, eugenol (Danforth)[26]; carbon disulfide, diethyl ether, toluene, iso-amyl alcohol (Chang)[28]; n-hexane (Mopsik)[29]; chlorobenzene, dichloromethane, ethyl acetate, isopropyl ether, tetrahydrofuran (Schornack and Eckert)[30]], with no readily observable correlation to structure. Resolving a possible physical significance of $S^{\ddagger}$ as it relates to temperature, hydrogen bonding (?), density, and concentration of molecular substances is a challenge.

B. Benzene behavior function only of density (25.7-400°C).

An example presented here is the excellent adherence to Eq. (9) of ε for pure benzene of Deul and Franck[23,24] from 25.7 to 400°C that shows its value depends only on density, and independent of temperature. Deul and Franck[23] noted this temperature

independence in giving a common curve (25.7-400°C) of ε plotted against ρ. Fig. 10 shows the Deul-Franck values of ε for pure benzene plotted as log (ε – 1) vs log ρ at temperatures from 25.7 to 400°C and from 0.1 to 300 MPa. Their results at each temperature fitted separately to Eq. (9) by NLLS[10] give values of $A^{\ddagger}$ and slope $S^{\ddagger}$ regularly changing only slightly with temperature (25.7-400°C), and closely describing the single straight line of Fig. 10. Values of $A^{\ddagger}$ and $S^{\ddagger}$ from Eq. (9) at the several temperatures together with deviations in fit are given in Table II for a potential significance in correlating with temperature. Also included are $A^{\ddagger}$ and $S^{\ddagger}$ from the combined fit of all values in Fig. 10 at 25.7-400°C. The very small standard deviations ($\Delta\varepsilon$ = 0.00037 to 0.0015) for the several temperatures greatly support not only the high quality of isothermal adherences to a single-straight line, 25-400°C, but also the excellent quality of dielectric constants obtained by Deul and Franck[23,24] who did not apply the form of Eq. (9).

C. Further justification for extrapolation to high densities by Eqs. (3) or (9)

The close adherence within experimental uncertainty of these pure organic liquids and shown here for benzene at extreme ranges of temperature and pressure (density) are presented to further justify that water at moderately high densities follows the same relationship through Eq. (3) as that of Eq. (9). These observations suggest conformity for water (and the organic liquids) at densities significantly higher than can be observed experimentally. The surprising commonality in behavior of pure benzene at all temperatures studied should be useful for future explanations that might be observed for other organics if their experimental values of ε were to become available.

In another paper[31] the simple density relationship of Eq. (9) is shown to describe dielectric constants of numerous liquids (fluids) compared with the limited descriptions by past theoretical equations derived from the Born theory and Tait expression.

VI. DISCUSSION

The observations in Fig.1 show that at all temperatures as the density of pure water approaches very low values, ($\varepsilon_w - 1$) approaches direct proportionality to ρ_w, that is, both $[\partial \log (\varepsilon_w - 1)/\partial \text{dog } \rho_w]_T$ and $[\partial (\varepsilon_w - 1)/\partial \rho_w]_T \rightarrow 1$. The number/volume of molecules is directly proportional to mass/volume, where each term can be considered a volume density. Ideally, the macroscopic dielectric constant would be expected to be proportional to this volume density of dipolar molecules. Fig. 2 shows that the (essentially) constant isothermal slope at volume densities above 0.25 g/cm^3 with rising temperature increases sharply from 1.0, near the lowest temperature of liquid metastability (-35^{o}C), to a much slowing increase near the critical temperature (374^{o}C) and approaches a limit of 1 2/3 as temperature rises higher. The value of this limiting slope equates ($\varepsilon_w - 1$) to a numerical proportionality to a volume density times a surface density, which equals $\rho^1\rho^{2/3} = \rho^{1\ 2/3}$. At high temperature and density the approach with rising temperature to this numerical proportionality experimentally applies, and one must speculate on its significance.

Perhaps the increase from an "ideal" slope for $[\partial \log (\varepsilon_w - 1)/\partial \log \rho_w]_T = 1$ at -35^{o}C to 1 2/3 at high densities and high temperature represents ultimate destruction of hydrogen-bonding structure and that the dielectric constant is now a function of a product of surface and volume concentrations. Below 100^{o}C strong (hydrogen) bonding may be the cause of much higher values of ε that may cause a major disappearance of the effect of surface density on ε. At very low densities, although bonding structure between molecules should become insignificant, the major effect on the value of ε should result from changing volume concentration as observed.

VII. CONCLUSION

By presenting a view of dielectric-constant behavior of water over extremes of temperature and density, showing agreement for behavior in both dioxane-water and benzene-water

solutions, simplicities become apparent that should be of interest to theoretical studies for their significance and application to the chemical-physical nature of water. Evaluated dielectric constants of water in dioxane-water and benzene-water solutions are shown to align with the behavior of pure water as a function of temperature and density. The Fernández, et al., IAPWS formulation for dielectric constant of water to extreme temperatures and densities has made possible a simple equation with a minimum of constants that fits well the IAPWS formulation. The equation is based on straight-line and eight limiting relationships that provide confidence in ease of extrapolation outside the range of experiment, mentioned as a need by Weingärtner and Franck in their recent review on supercritical water.[32]

The critical evaluation of the dielectric constant of water by Fernández, et al., as adopted by IAPWS provides authoritative values, with Eq. (2) presented here considered because of its simplicity. Either, however, provides the same results within stated uncertainties.

With Eq. (2), it would seem that any new theory would have to accept the framework of these observed simple physical relationships (Occam's razor). As Ball[33] recently concluded in "Water – an enduring mystery": "Water reminds us of the dangers of doing science in silos, the risks of leaving apparently tidy explanations unexamined, the importance of not letting ubiquity lead to invisibility, and the recognition that new ways of studying the world can exacerbate as well dispel confusion." It would seem that the equation presented here responds to his comments.

ACKNOWLEDGMENTS

This paper is dedicated to the memory of my late wife, Joanne Fox Marshall, who supported and inspired me strongly over half a century in all my endeavors for which I am extremely grateful. I would like to acknowledge the generous support over the decades by

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Table I. Comparisons of dielectric constants by Eq. (2) with those (ε_{pred}) at various state points in Table 9 of Fernández, et al.[5] and by IAPWS[8] ; selected comparisons from Bradley and Pitzer[13] formulation. U_ε = estimated absolute uncertainty in ε_{pred}.

P/MPa	*T*/K	ρ/(g cm^{-3})	ε_{pred}[5,8]	ε [Eq. (2)]	U_e[5,8]	ε_{pred} - Eq. (2)
P_o[a]	238[b]	0.97506[c]	106.31	103.26	1	+3.05[d]
P_o[a]	256[b]	0.99525	95.20	95.23	0.3	-0.03
P_o[a]	273	0.99983	87.96	87.87	0.04	+0.09
585.3	273	1.180	107.06	106.15	0.05	+0.91[d]
P_o[a]	323	0.98810	69.96	69.59	0.04	+0.37
1189	323	1.253	97.02	94.29	0.04	+2.73[d]
P_o[a]	373	0.958	55.57	55.33	0.2	+0.24
495.8	373	1.110	67.73	67.58	0.5	+0.15
3.16541	510	0.0158320	1.122	1.127	0.003	-0.005
141.68	523	0.900	32.23	32.37	1	-0.14
14.757	614	0.0943	1.77	1.75	0.02	+0.02
22.0386	647	0.357[e]	6.17	6.56	0.3	-0.39
19.9337	673	0.100	1.75	1.70	0.1	+0.05
407.896	673	0.900	23.60	23.66	0.5	-0.06
27.099	773	0.100	1.66	1.57	0.2	+0.09
581.908	773	0.900	20.16	20.19	0.5	+0.03
124.707	873	0.450	6.28	6.47	0.4	-0.19

(Continued on next page)

Continued from previous page (Table 1)

P/MPa	T/K	ρ/(g cm^{-3})	ε_{pred}[5,8]	ε [Eq. (2)]	U_e[5,8]	ε_{pred} - Eq. (2)
Bradley-Pitzer[13] values in Table 7 of Fernández, et al.[5] compared with Eq. (2) values:						
P_o[a]	238[b]	0.975	102.69	103.26	- -	-0.57
"	"	"	(106.31)[f]			(+3.05)[f]
1000	273	1.267	114.23	115.14	- -	-0.91
"	"	"	(117.73)[f]			(+2.59)[f]
1000	298	1.239	101.11	101.83		-0.72
"	"	"	(104.60)[f]			(+2.77)[f]

[a] P_o = liquid state at 0.101325 MPa.

[b] Metastable liquid; ice is stable form at this T and P.

[c] All significant figures as given in references.

[d] Compare with Bradley-Pitzer values in same regions below (see text).

[e] 0.322 g cm^{-3} is value at critical point.[9] Using 0.322 and 647 K with Eq. (2) gives ε = 5.73 compared to the Fernández, et al., (IAPWS) formulation[5] value extrapolated-interpolated from their Table 20 of 5.36, or $\Delta\varepsilon$ of – 0.37.

[f] Values by Fernández, et al., formulation[5] in their Table 7.

Table II. Constants for Eq. (9)[a] giving close straight-line fits for the dielectric constants (ε) of benzene of Deul and Franck[23,24] from 25.7° to 400° C and to 300 MPa.

t/°C	NDP[b]	$A^{\ddagger}$	$S^{\ddagger}$	Δlog (ε - 1)[c]	Δε (Max.)
25.7	12	0.1781	1.241	0.00025	0.0017
50.0	18	0.1772	1.240	0.00016	0.0008
75.0	25	0.1767	1.245	0.00026	0.0015
100.0	32	0.1758	1.244	0.00027	0.0019
150.0	34	0.1736	1.236	0.00033	0.0024
200.0	35	0.1726	1.233	0.00030	0.0020
250.0	29	0.1704	1.220	0.00056	0.0027
300.0	34	0.1691	1.214	0.00061	0.0026
350.0	35	0.1683	1.211	0.00065	0.0036
400.0	32	0.1676	1.210	0.00057	0.0032
Entire temperature-pressure range combined (Fig. 4):					
25.7-400	54	0.1753	1.245	0.0023	0.011

[a] Eq. (9): $\log(\varepsilon - 1) = A^{\ddagger} + S^{\ddagger} \log[\rho/(\mathrm{g\ cm^{-3}})]$

[b] Number of data points.

[c] Standard deviation.

LIST OF FIGURES

Fig. 1. Log ($\varepsilon - 1$) vs. log ρ (water) over wide ranges of density and temperature evaluated from compilations of Fernández, et al. (1997), -35° to 927°C, with extensions to low densities for ε (water) in dioxane-water 25-300°C) and benzene-water (300-400°C) solutions (Section IV, Figs. 5-9). Lines from Eq. (2).

Fig. 2. The slope S, $[\partial \log (\varepsilon - 1) / \partial \log \rho/(\text{g cm}^{-3})]_T$, for water vs. temperature (°C) at densities above 0.25 g cm^{-3} (Eq. 3) applying dielectric constant (ε) compilations of Fernández, et al. (1997).

Fig. 3. Deviation plot for dielectric constant (ε) of water, $\Delta\varepsilon$ [IAPWS Eq. – Eq.(2)(text)] vs. ($\varepsilon - 1$) ; – 17 to 927°C, 0.1-500 MPa.

Fig. 4. Log polarization affinity (PA) vs 1/(T/K) at several constant densities (text).

Fig. 5. Log function describing dielectric constant (ε_w) of water in dioxane-water (25-300°C to 400 MPa) and benzene-water (300°C to 170 MPa) solutions and water (to 1000 MPa) vs. log density (water) in solution or pure water. $\varepsilon_w = \varepsilon$ (water), $\varepsilon_{obs} = \varepsilon$ (solution or pure water), $\varepsilon_{po} = \varepsilon$(pure dioxane or benzene), X_o = weight fraction organic in solution, $G = 1 + F\rho_w$; $F = 0$ (dioxane) or 5 (benzene). Lines from Eq. (2).

Fig. 6. Log function describing (ε_w) of water in benzene-water solutions (400°C, to 280 MPa) and pure water (400°C, to 1000 MPa) vs. log ρ(water) in solution or pure water. $\varepsilon_{obs} = \varepsilon$ (solution or pure water); $\varepsilon_{po} = \varepsilon$(pure benzene, X_o = weight fraction benzene. $G = [(1 + F\rho_w/\text{g cm}^{-3})]$ with $F = 5$ for benzene.

Fig. 7. Log (ε_w – 1) at 50°C of water in dioxane-water solutions at vapor saturation and of pure water at 50, 387 and 927°C up to 1000 MPa vs. log ρ (water)/(g/cm^3). Correction for ε_{po} unnecessary above 0.25 g cm^{-3}.

Fig. 8. Expanded region: straight-lines describing log (ε_w – 1) of water in dioxane-water (25 – 300°C to 400 MPa) and benzene – water (300°C to 170 MPa) solutions and water to 1000 MPa vs. log [density H_2O/(g cm^{-3}) in solution or pure water. Correction for dioxane unnecessary above 0.25 g cm^{-3}.

Fig. 9. Deviation plot for dielectric constant (ε_w) at 25° and 50°C of water in dioxane-water solutions (0.1 MPa) and of pure water (to 1000 MPa), $\Delta\varepsilon_w$ [Eq. (6) – Eq. (2)] vs. (ε_w – 1), showing agreement over the extreme range of dielectric constant and density. G = 1 for dioxane; thus Eq. (8) unnecessary.

Fig. 10. Single straight-line function [log (ε – 1)] of dielectric constant (ε) of pure benzene vs log [density/(g cm^{-3})] at 26-400°C and pressures to 300 MPa independent of temperature.

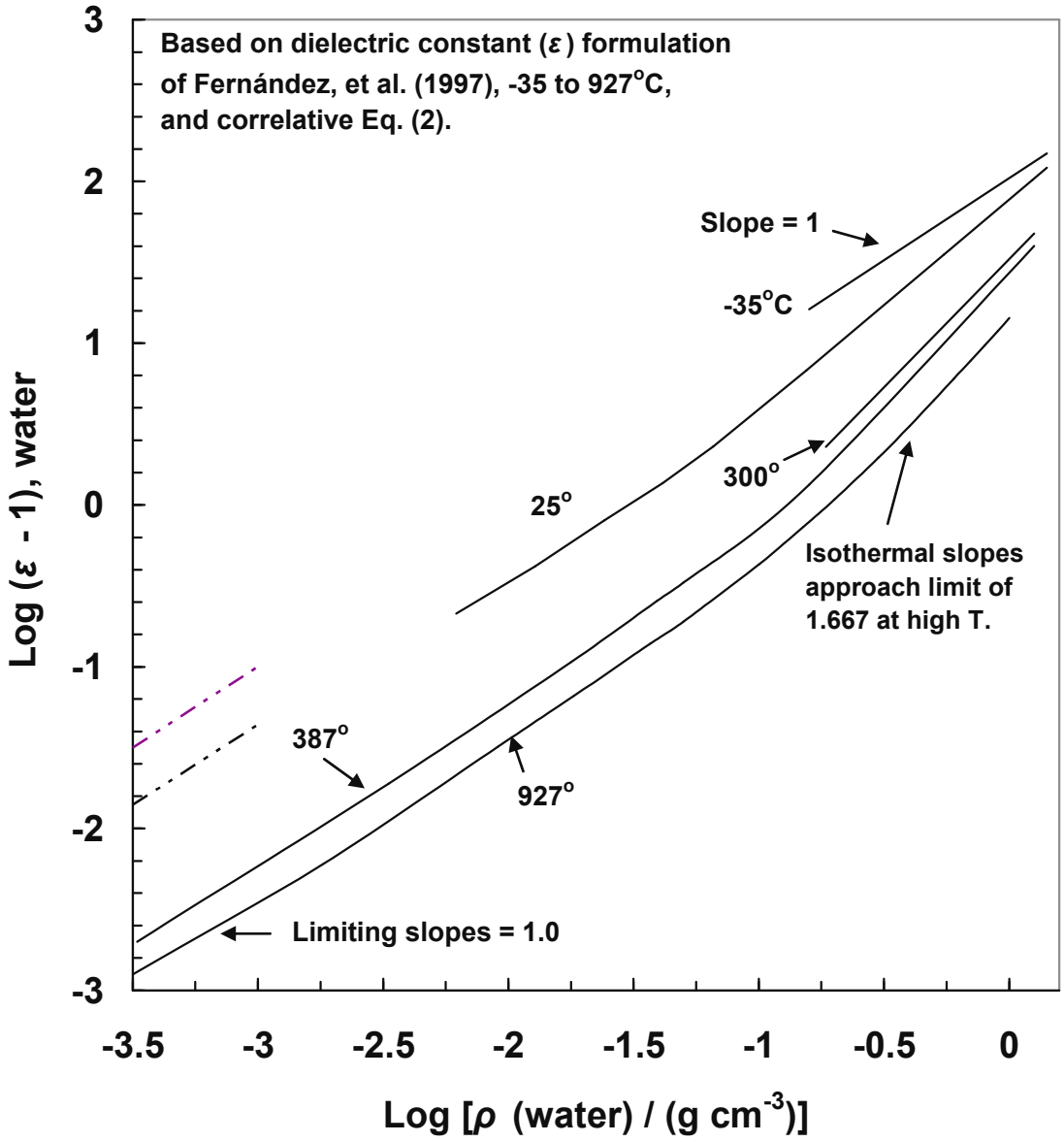
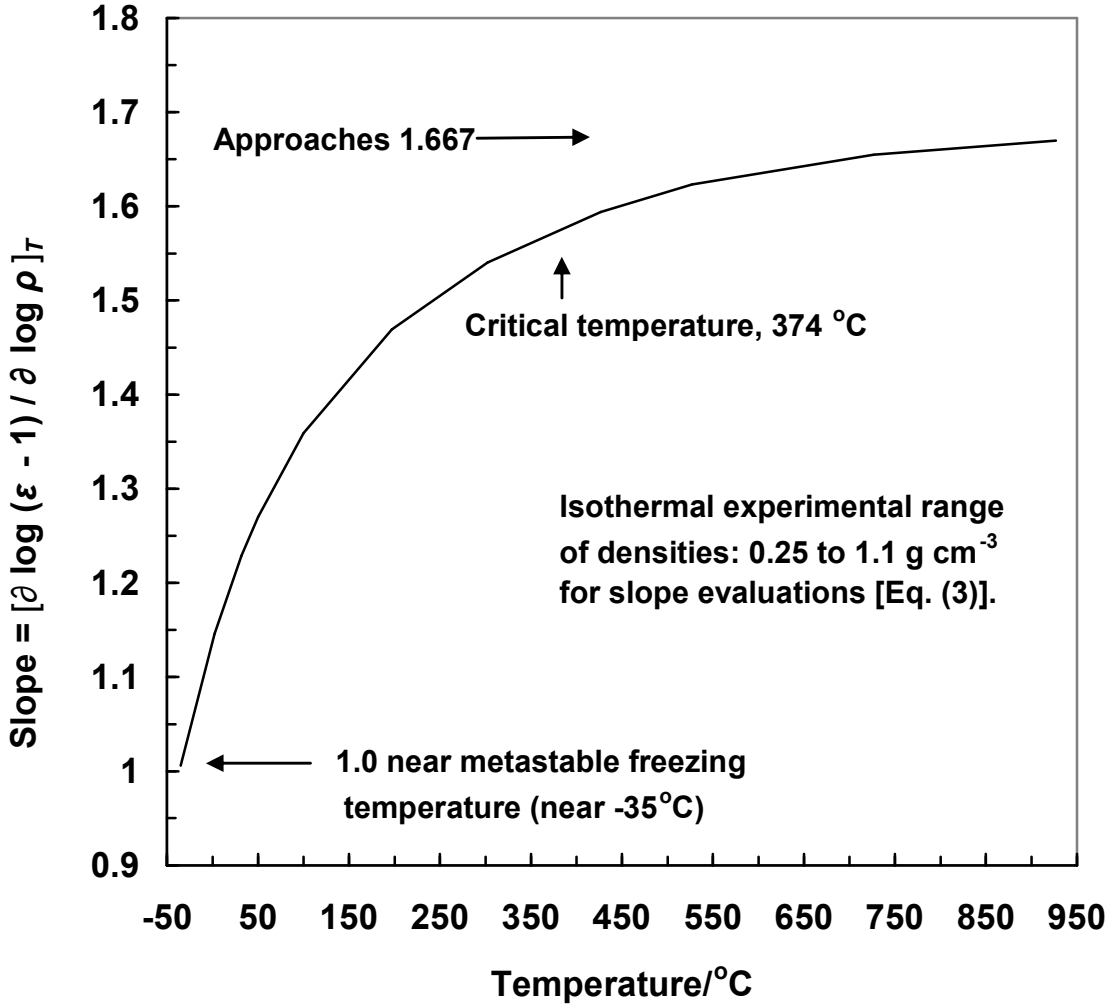


Fig. 1. Log (ε - 1) vs. log ρ (water) over wide ranges of density and temperature evaluated from compilations of Fernández, et al.(1997), -35° to 927°C, with extensions to low densities at 25-400°C for ε (water) in dioxane-water (25-300°C) and benzene-water (300-400°C) solutions (Sect. IV, Figs. 5-9). Lines from Eq. (2).



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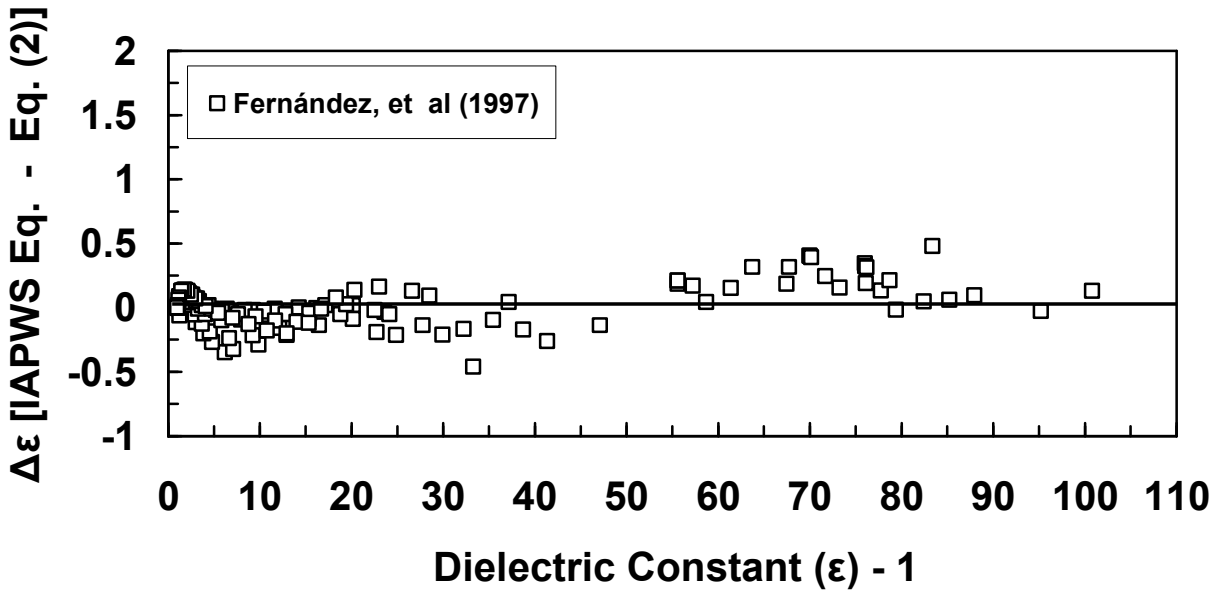

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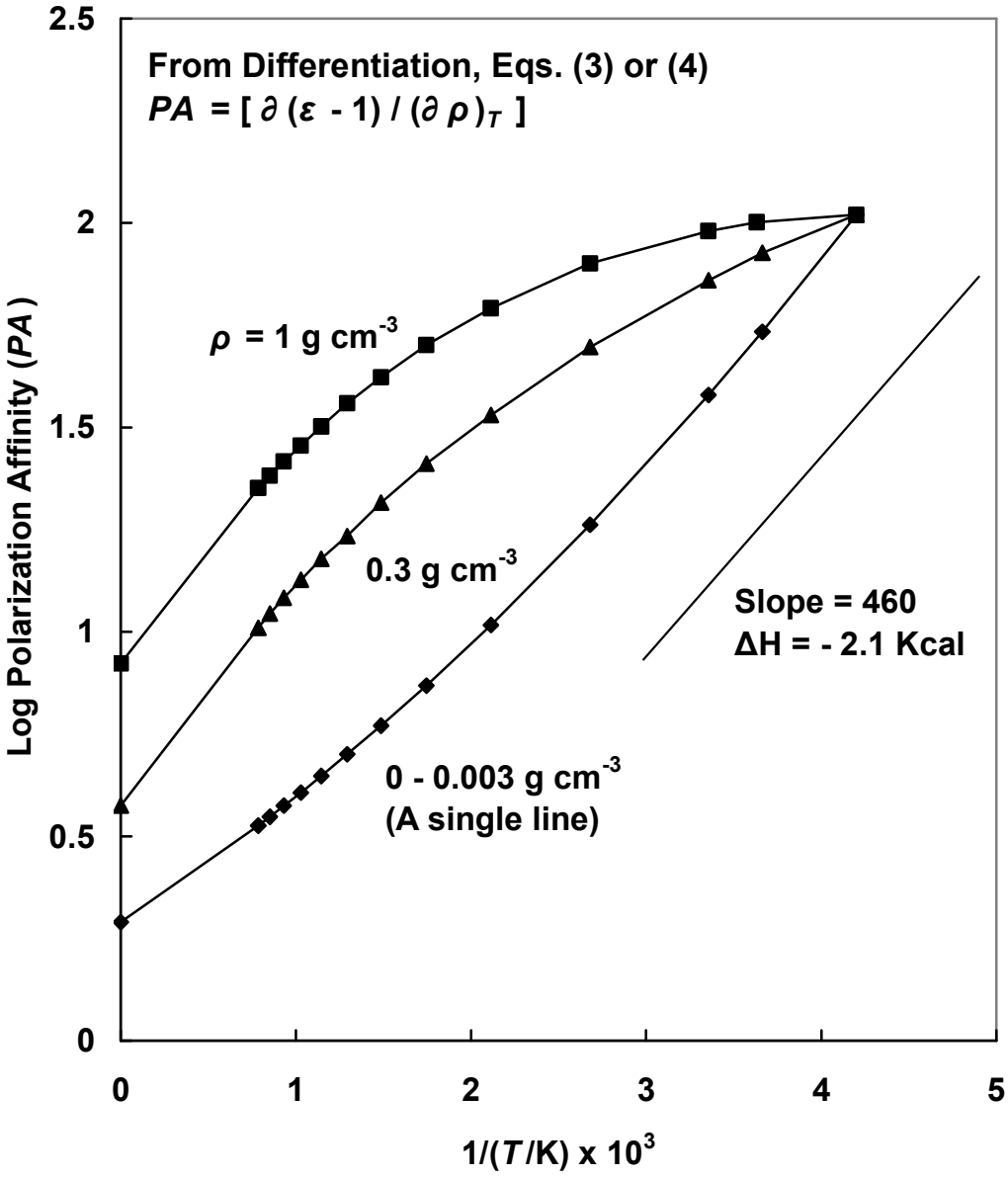

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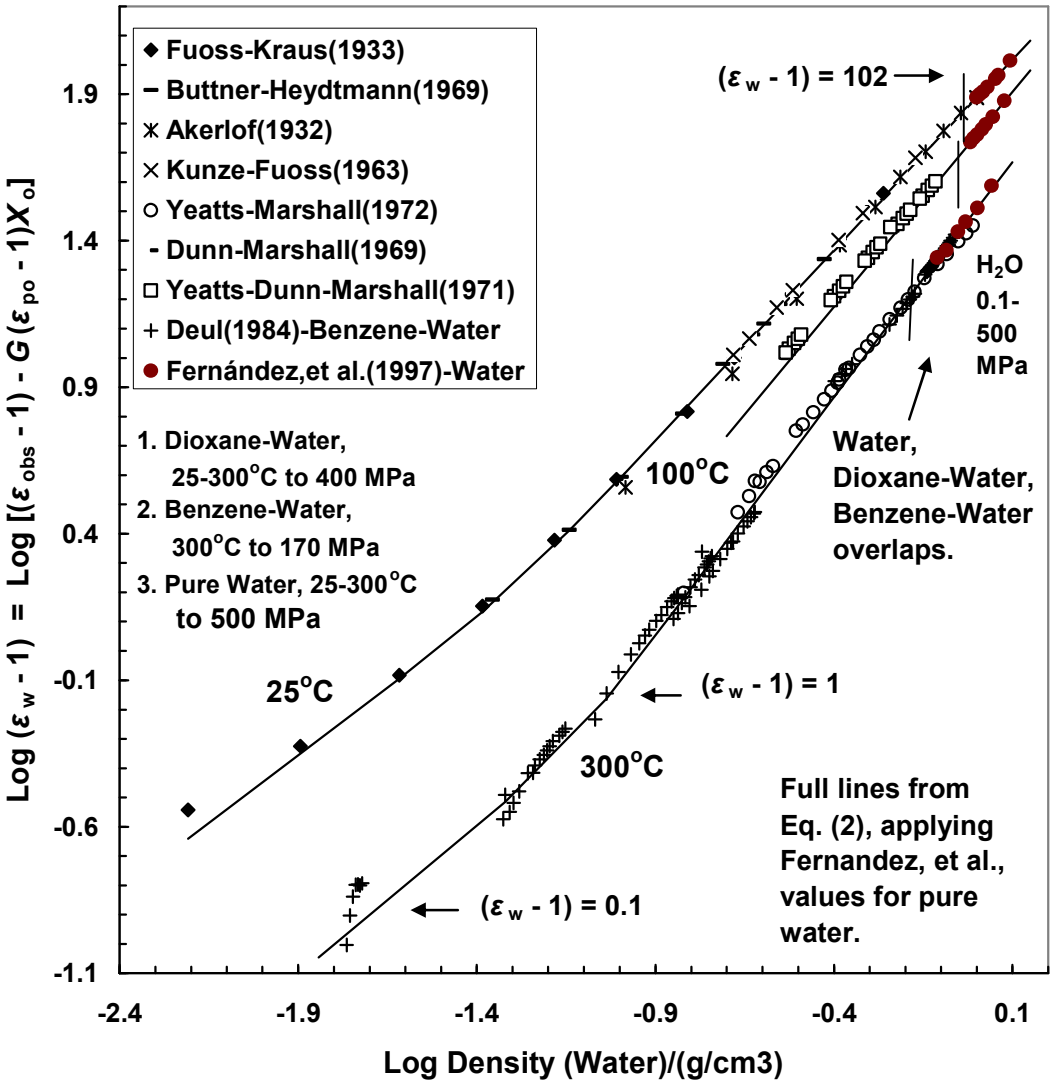

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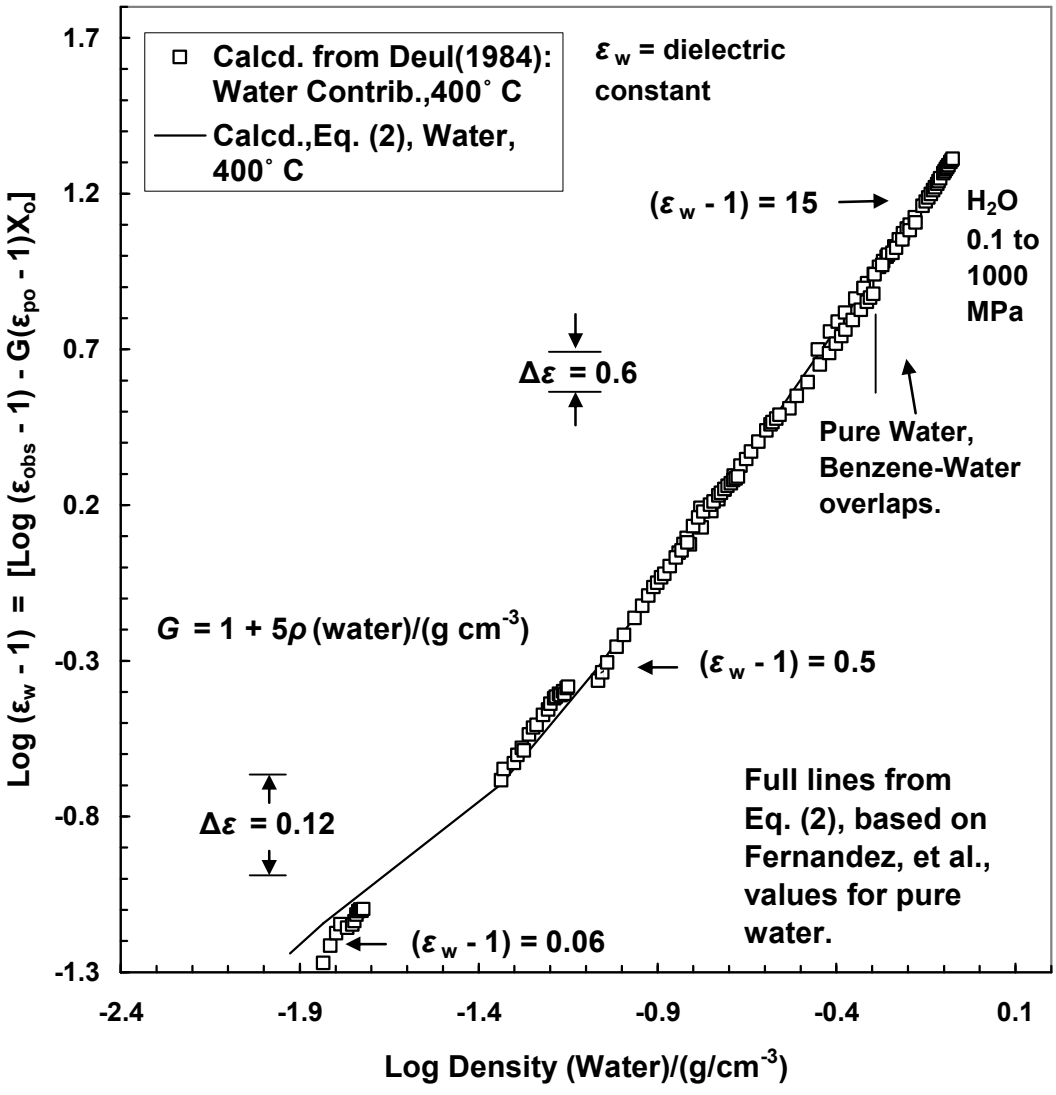
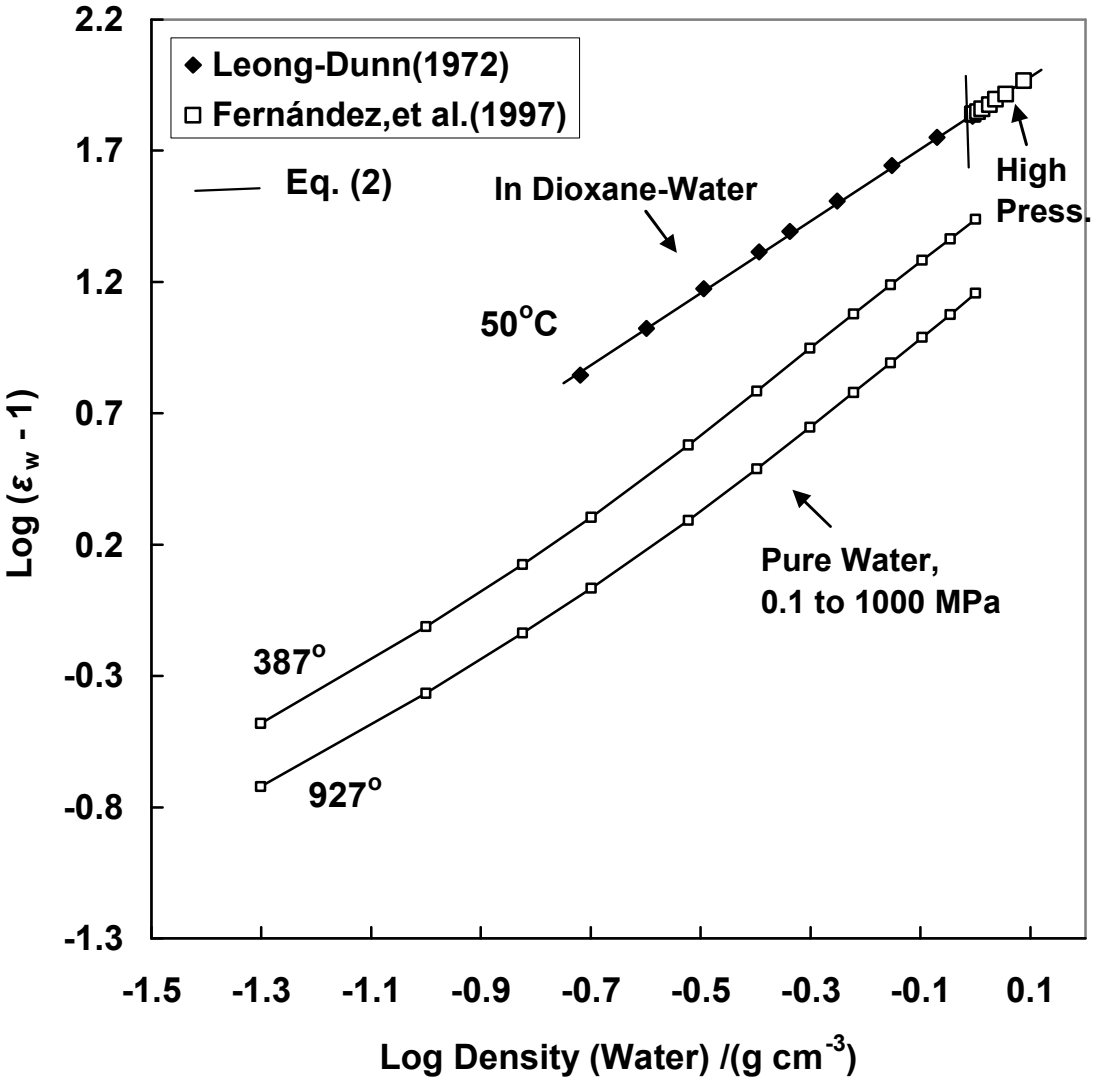


Fig. 6. Log function describing ε_w (water) in benzene-water to 280 Mpa and pure water to 1000 Mpa at 400°C vs. log density (water, ρ_w) in solution or pure water; $\varepsilon_{obs} = \varepsilon$ (solution or pure water); ε_{po} = (pure benzene); X_o = Wt. Fract. benzene. $G = [1 + F\rho_w/(\text{g cm}^{-3})]$ where $F = 5$ for benzene.



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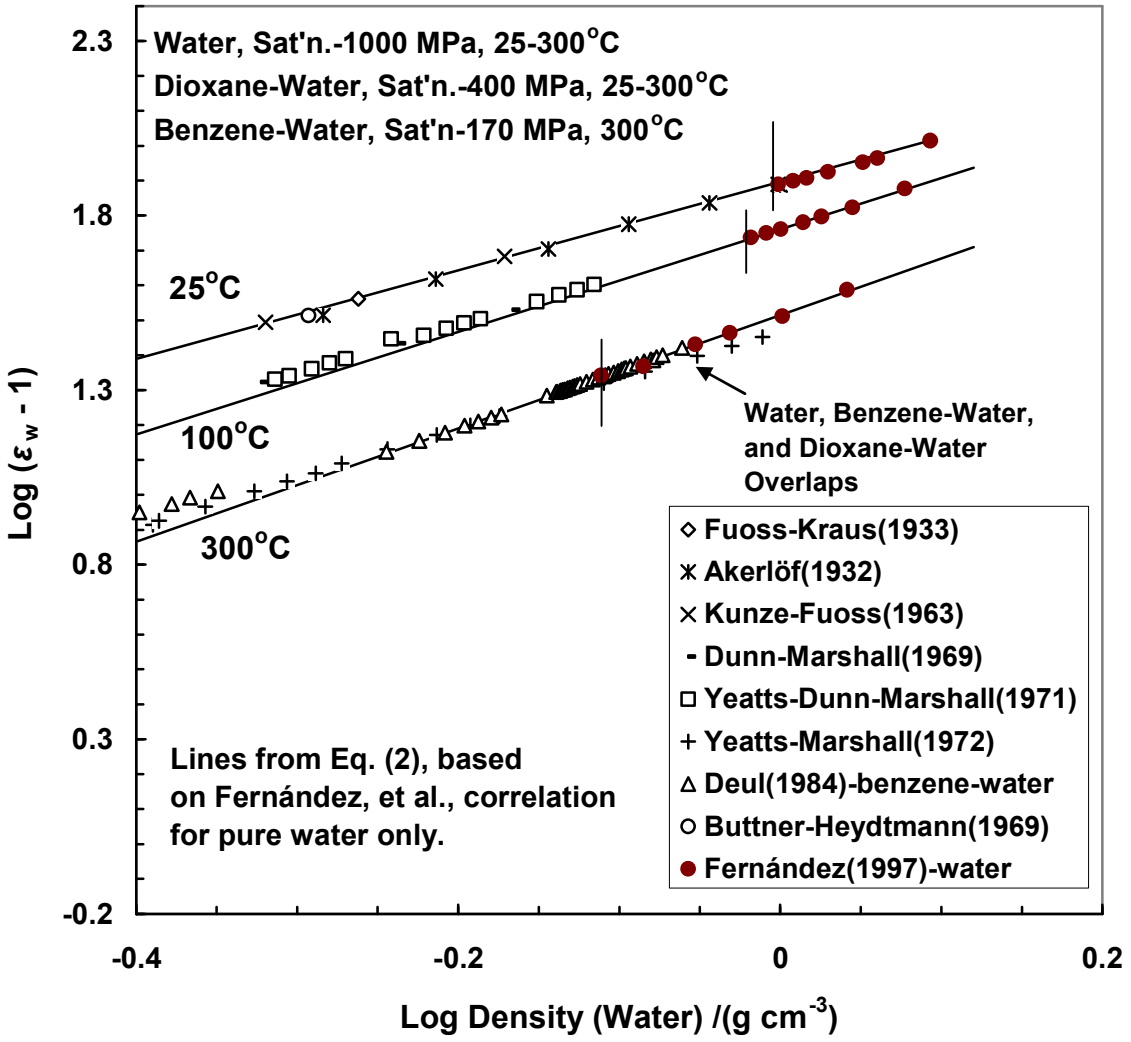

Fig. 8. Expanded region: straight-lines describing log (ε_w - 1) of water in dioxane-water (25 - 300°C to 400 MPa) and benzene-water (300°C to 170 Mpa) solutons and water to 1000 MPa vs. log density water in solution or pure water. Correction for dioxane unnecessary above 0.25 g cm^{-3} water.

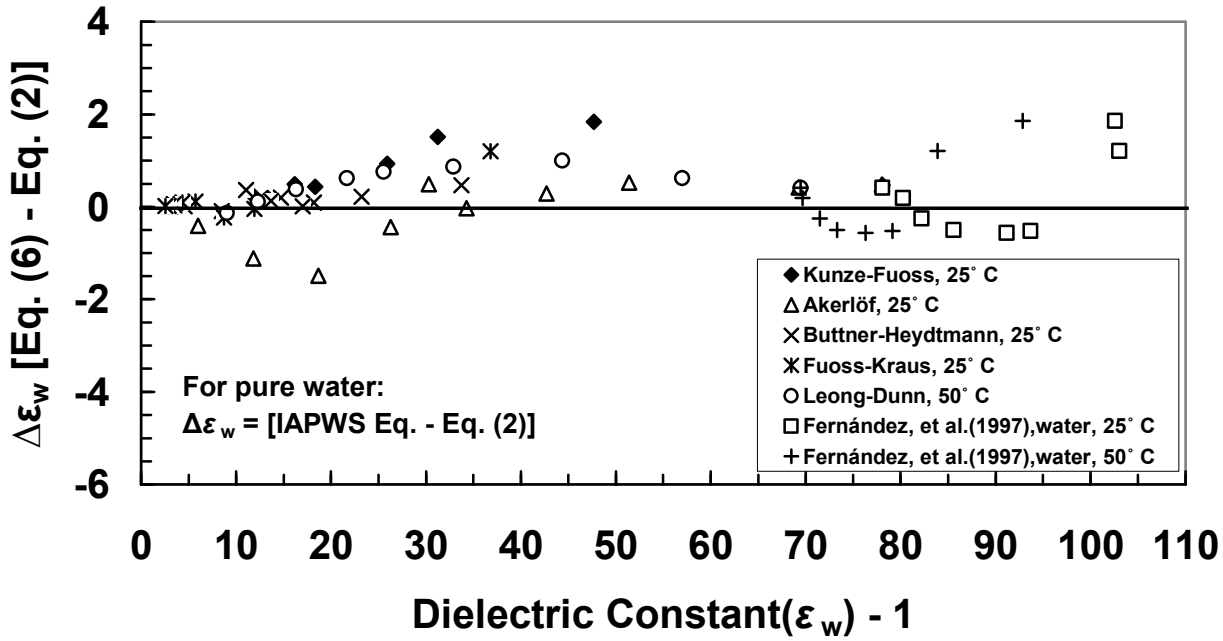

Fig. 9. Deviation plot for dielectric constant (ε_w) of calculated water in dioxane-water solutions at 25° and 50°C, 0.1 MPa, and water to 1000 MPa; $\Delta\varepsilon_w$ [Eq. (6) - Eq. (2) (text)] vs. (ε_w - 1). G = 1 for dioxane; Eq. (8) unnecessary.

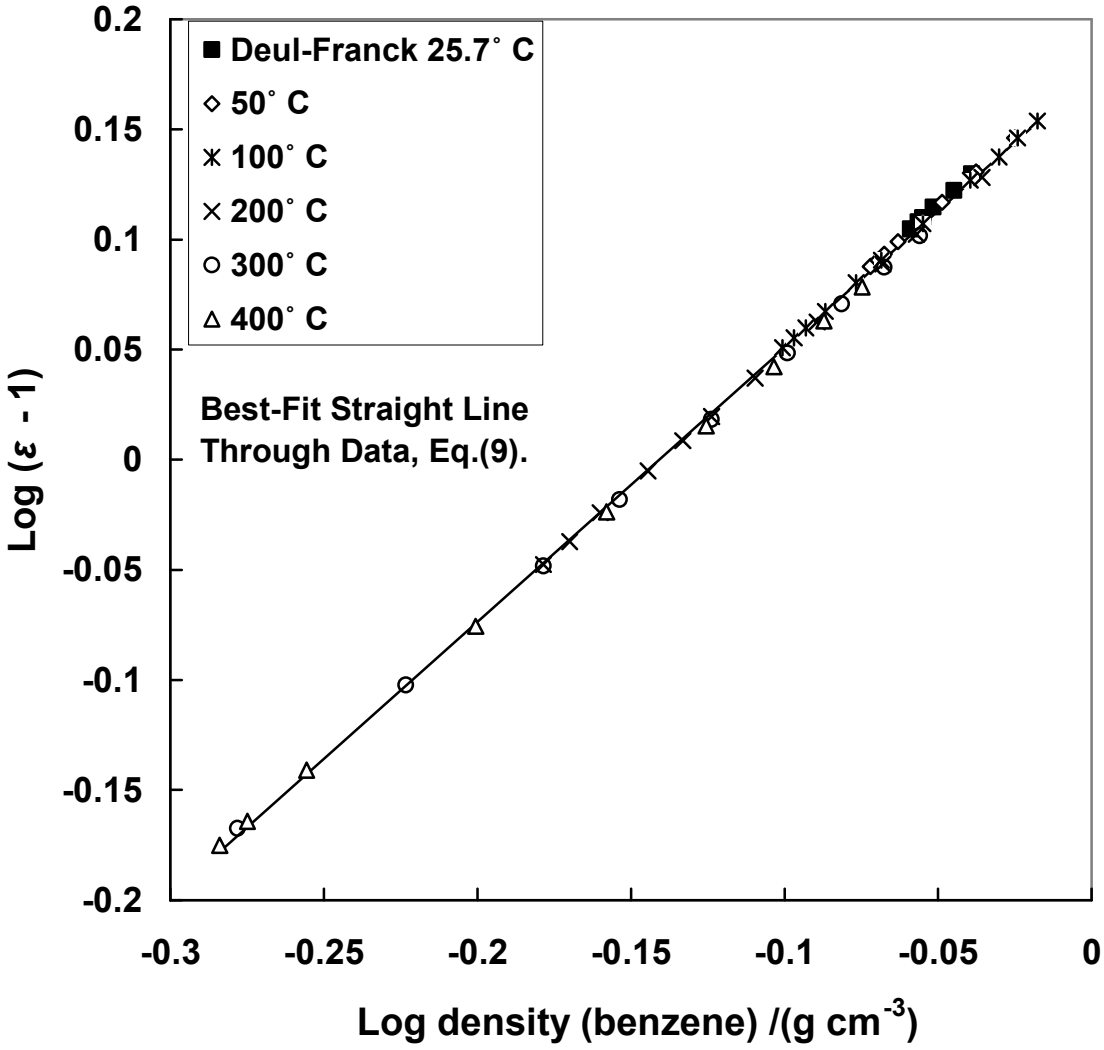

Fig. 10. Single straight-line function [log (ε - 1)] of dielectric constant (ε) of pure benzene vs. log [density/ (g cm^{-3})] at 26-400^{o}C and pressures to 300 Mpa independent of temperature.